Electron Irradiation of Dilute Aqueous Solutions of Polymers over a Range of Temperatures

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Dilute aqueous solutions of carboxy methyl cellulose (CMC) and gelatin were irradiated with 1 MeV electrons over the temperature range from $+25°C$ to very low temperatures, -70 to $-170°C$. The effects, chain scission in CMC and cross linking in gelatin, were measured by determining the viscosity change of CMC solutions and the insoluble gel fraction produced in gelatin solutions. For both solutions there was a great change in the effect near the freezing temperature, but there were some differences in behavior between the two materials. With CMC there was a sharp break near $0°C$ with the rate of change 37 times as great above $0°C$ as below $0°C$; there was apparently no change from $\sim 0°C$ down to $-170°C$. With gelatin the change was somewhat more gradual near freezing. The rate was 7.5 times as great at $+5°C$ as at $-5°C$, with a continual change over that temperature range and a continuing change in rate down to $-70°C$. The cross linking rate depends on the mobility of the polymer chains and apparently for gelatin solutions the mobility continues to decrease as the temperature is lowered below freezing.

L'IRRADIATION ELECTRONIQUE DES SOLUTIONS DILUÉES AQUEUSES DE POLYMÉRES À TRAVERS UNE GAMME TE TEMPÉRATURES

Des solutions aqueuses diluées de carboxy-méthyl-cellusose (CMC) et de gélatine furent irradiées d'électrons de 1 MeV à travers la gamme de températures de $+25°C$ à des températures très basses, -70 à $-170°C$. Les effets, soit la scission de chaînes dans le CMC et les raccords en travers dans la gélatine, furent mesurés en mesurant le changement de viscosité des solutions CMC et la fraction de gel insoluble produite dans les solutions de gélatine. Pour toutes deux solutions il y avait un grand changement d'effet près de la température de glace, mais il y avait quelques différences de comportement entre les deux matériaux. Avec la CMC il y avait une forte différence prés de $0°C$ avec le taux de changement 37 fois plus grand dessus de $0°C$ qu'au dessous; il ne paraissait pas y avoir de changement de $\sim 0°C$ jusqu'à $-170°C$. Avec la gélatine le changement fut un peu graduel auprès du gel. Le taux fut 7,5 fois plus grand à $+5°C$ qu'à $-5°C$, avec un changement continu à travers cette gamme de température et un changement de taux continu jusqu'à $-70°C$. Le taux de raccords en travers dépend de la mobilité des chaînes polymériques et il semble que pour les solutions de gélatine la mobilité continue à s'affaiblir avec l'abaissement de la température au dessous du gel.

ЭЛЕКТРОННОЕ ОБЛУЧЕНИЕ РАЗВЕДЕННЫХ ВОДНЫХ РАСТВОРОВ ПОЛИМЕРОВ ПРИ РАЗЛИЧНЫХ ТЕМПЕРАТУРАХ

Разведенные водные растворы карбоксиметилцеллюлозы (СМС) и желатина облучались электронами в 1 мэв при температурах от $+25°C$ до очень низких от -70 до $-170°C$. Результаты, т.е. деление цепи в СМС и образование поперечных связей в желатине, измерялись определением изменений вязкости растворов СМС и нерастворимых

фракций геля полученных в растворах желатина. Оба раствора резко изменялись под действием близких к замерзанию температур, но отмечены некоторые различия между поведением обоих материалов. В растворах СМС был резкий разрыв около 0°C со скоростью в 37 раз бо́льшей при температуре выше 0°C, чем ниже 0°C, а от ∼0°C вниз к −170°C, повидимому, не было изменений. Желатин давал постепенные изменения, приближаясь к точке замерзания. Скорость изменения была в 7,5 раз бо́льшей при +5°C, чем при −5°C, причем изменения продолжались при этом диапазоне температур и далее до −70°C. Скорость образования поперечных связей зависит от подвижности цепей полимера и, повидимому, подвижность в растворах желатина продолжает уменьшаться при температурах ниже точки замерзания.

ELECTRONENBESTRAHLUNG VERDÜNNTER WÄSSERIGER LÖSUNGEN VON POLYMEREN IN EINEM TEMPERATURBEREICH

Verdünnte wässerige Lösungen von Carboxymethyl-Zellulose (CMZ) und Gelatine wurden mit 1 MeV Elektronen im Temperaturbereich von +25°C bis zu sehr tiefen Temperaturen, −70 bis −170°C bestrahlt. Die Wirkungen, eine Kettenreaktion im CMZ und eine Querverkettung in Gelatine, wurden durch Bestimmung der Viskositätsänderungen der CMZ-Lösungen und der unlöslichen in Gelatinelösungen entstandenen Gelfraktion gemessen. Die Auswirkung änderte sich stark für beide Lösungen in der Nähe des Gefrierpunktes, aber es bestanden einige Unterschiede im Verhalten zwischen den beiden Substanzen. Bei CMZ trat ein scharfer Knick bei 0°C auf, wo die Änderungsgeschwindigkeit oberhalb 0°C 37 mal grösser war als unterhalb 0°C; von 0°C bis zu −170°C trat anscheinend keine Veränderung ein. Mit Gelatine war die Veränderung in der Nähe des Gefrierpunktes etwas allmählicher. Die Geschwindigkeit war $7\frac{1}{2}$ mal höher bei +5°C als bei −5°C mit einer anhaltenden Änderung in diesem Temperaturbereiche und einer fortlaufenden Änderung der Geschwindigkeit bis auf −70°C herunter. Die Querverkettungsgeschwindigkeit hängt von der Beweglichkeit der Polymerketten ab und die Beweglichkeit scheint für Gelatinelösungen dauernd abzunehmen, wenn die Temperatur unter den Gefrierpunkt fällt.

INTRODUCTION

THE EFFECTS of high energy electrons on polymers may be either direct or indirect. The direct effect, caused by collision of the electron with the molecule may result in ionization by capture or removal of an electron or in excitation, perhaps followed by ionization or breakage of inter atomic bonds with formation of free radicals. The indirect effect results from the chemical action of free radicals, hydrogen peroxide, solvated electrons or other active agents produced in other materials in contact with the polymer, e.g. the solvents in which the polymers are dissolved. The indirect effect is especially great in water solutions. In such solutions it can be reduced greatly by decreasing the mobility of the active agents, for example, by lowering the temperature below the freezing point. This has been done for a variety of molecular species in water, serum albumin,[1] pepsin,[2] DNA,[3] ascorbic acid,[4,5] nicotinamide,[5] and bacteria such as *E. Coli*,[6] *salmonella*[3] and *staphyococcus aureus*.[2] The effect is generally the same, a much reduced effect when frozen and this has generally been interpreted as indicating very little or no indirect effect frozen and combined indirect and direct effect unfrozen with the indirect effect predominating.[8,9] There are exceptions however; for example, the effect on bacterial spores is not significantly reduced when frozen. Also, with certain molecular structures the effect is largely direct at room temperature, as in the irradiation of homocyanin with α particles.

In our laboratory the dye, the sodium salt of dimethoxy diphenyl diazo bis amino 1 naphthol 5,7 sulfonic acid, in cellophane and in water,[10] was irradiated with 1 MeV electrons. The amount of water in cellophane was small, not more than 5 per cent, but even so, on freezing the rate of bleaching of the dye was only about 40 per cent that at room temperature. As a 0.25% solution in water, the rate of bleaching was about 10 times that in cellophane and on freezing this was reduced to ∼ 1/450 the rate at room temperature.

For the present work, we selected carboxy methyl cellulose (CMC) and gelatin as water soluble polymers in which the direct and indirect mechanisms could be separated by varying the temperature. The experiments were planned on the assumption that with CMC all or nearly all the effect would be chain scission and with gelatin the effect would be mainly or wholly cross linking. The materials were irradiated in dilute aqueous solutions, generally 1–3 % concentration and the changes were determined by measuring the viscosity for CMC and the gel fraction for gelatin.

PREPARATION AND IRRADIATION OF SAMPLES

The samples were solutions in water, with concentrations varying from 1 to 5 % by weight. The carboxy methyl cellulose was "Hercules Powder Company, Type 4"; the gelatin was "Atlantic Pure Food Gelatin, 100 Bloom, Type B". The samples were prepared by simple solution in distilled water, either at room temperature or warmed slightly. A preservative, 1 part in 500 of 1 % merthiolate solution, was added to the gelatin samples. The solutions were contained in flasks with small glass tubes inserted in rubber stoppers adjustable in height so that as desired (1) gas, either argon or oxygen, could be bubbled through the solution or (2) the gas pressure could be used to force the solution out of the flask into the cell used for irradiation.

Irradiation cell

The irradiation cell was made of aluminum as shown in Fig. 1. The sample space was 30.5 cm long, 3.8 cm wide and 0.23 cm deep. The top of the cell was a 0.01 cm-thick sheet of aluminum held in place with the rubber gasket and the 1.3 cm-thick aluminum frame.

Before filling, the cell was flushed with the appropriate gas. By adjusting stop cocks the solution was slowly forced into the cell and when it exuded the threaded inlet and outlet plugs were closed. The latter were located to insure that all of the sample was irradiated.

Irradiation

The electron source was a High Voltage Engineering Company Model JS, 1 MeV vertical beam Van de Graaff electron generator. The beam exited through a long 0.1 cm-thick aluminum window. The sample was carried under the beam on a conveyor belt, with the long dimension in the direction of motion. The electron beam oscillated 200 cps in a vertical plane perpendicular to the sample motion, i.e. in the direction of the exit slot, by coils around the exit tube. The dose was varied by changing the belt speed in the range from 1.6 to 8 cm/sec and the number of passes under the beam.

In the cell the top aluminum sheet (density 2.7 g/cm^3) was equivalent to 0.007 cm of water; the bottom of the sample was at an equivalent depth of 0.237 cm of water; measurements and calculations of the dose distribution in water show that, neglecting the small amount of solute and the back scatter from the bottom of the cell, the relative dose is 0.55 at the top surface of the sample, and 0.80 at the bottom of the sample compared to 1.0 at a depth of 0.175 cm. The maximum variation in dose throughout the sample is ± 23 per cent. Integration of the dose depth curve indicates that of the electrons penetrating the surface of the aluminum sheet, the fraction 0.78 is absorbed in the sample. In all cases the electron beam was adjusted to 100 μA. Measurement of the deflection of the beam indicates that at a setting of 50, the fraction 0.31 is incident on the width of the sample, i.e. the fraction 0.69 falls outside the sample. Then a current of $\sim 24.3 \mu$A is absorbed in the sample. At 1 MeV this is 2.43×10^8 ergs. At a belt speed of 2 cm/sec the energy absorbed by the sample is 1.39×10^8 ergs/g. The exposure then is $\sim 1.4 \times 10^6$ rad per pass. The dose varies inversely as the speed.

The primary purpose of this work is to determine the effect of change of state and temperature on the effectiveness of electron irradiation. The temperature was measured with a copper constantan thermocouple inserted in a small hole in the aluminum base of the sample cell. There was no automatic control of temperature but as the need for better control became apparent, more attention was paid to the drift with time. Longer cooling periods were used to reduce the effect of the lag and the temperature was measured before and after irradiation. For multiple pass exposures the irradiation was

interrupted to allow cooling to overcome the electron heating and the temperature changes were monitored during the rest periods. For some of the earlier tests the temperature was not measured; the values were close to dry ice and liquid nitrogen temperatures but later work showed this to be uncertain although the temperatures were considerably below freezing.

EVALUATION OF THE EFFECT OF IRRADIATION

Carboxy methyl cellulose

The changes effected in CMC were expressed as the change in viscosity of the solutions. The measurements were made with calibrated Ostwald tubes, numbers 100 and 200, which are intended for samples in the range 0.015 and 0.1 centistokes/sec. The samples were irradiated at concentrations of 1 and 3%. The viscosity was measured directly on the 1% sample and the other samples were diluted to 1% for measurement. After this measurement the concentration was measured by drying. Since the deviations from 1% were small, the correction could be made by assuming a linear dependence on concentration.

Gelatin

The changes effected in gelatin were expressed as the amount of insoluble gel fraction produced. The procedure varied somewhat but the following describes what we consider the best of the methods used. The irradiated sample was weighed, then poured into weighed stainless steel tubes and centrifuged at 10,500 rev/min for 40 min. No temperature control was exercised and the samples warmed from 24 to 30°C. The supernatant solution was poured into a weighed aluminum drying dish. The insoluble fraction was washed with the addition of distilled water and the centrifuging process repeated twice. The solid content of both samples was determined by drying at 50–60°C. The insoluble gel fraction was the value of interest. The two measurements provided a check on the operation. The total weight collected was usually a few per cent lower than expected from the initial weight of the sample.

RESULTS

Carboxy methyl cellulose

Thixotropy. CMC solutions show marked thixotropy. Flow through the viscometer was usually sufficient to reduce the viscosity; similar results were obtained by shaking in a bottle. On cooling to below freezing and on heating above room temperature, increases in viscosity remain after returning to room temperature. For one sample after freezing, heating and relaxing, the viscosity at 25°C varied from 28.9 to 39.2 centistokes. After considerable agitation the values varied from 28.9 to 33.4 centistokes. This introduces some uncertainty but fortunately the changes effected by irradiation are large compared to this uncertainty. In all the measurements, agitation and successive passages through the capillary were continued until fairly constant results were obtained.

Preliminary tests. Some preliminary results are summarized in Fig. 2 in which the viscosity is plotted vs. dose, expressed as the number of passes under the beam at a speed of 2 cm/sec.

The striking effect is the great difference between the effect above and below 0°C, for both 1 and 3% solutions. The samples were either at room temperature or were cooled with dry ice. The temperature was not well controlled but the samples were either definitely liquid or frozen.

The change in viscosity is a disproportionate measure of the effect of irradiation. Moreover, at high doses, the viscosity tends to approach that of water. If the viscosity is converted to specific viscosity and then to a "specific fluidity", $1/(\eta/\eta_w - 1)$ where η is the viscosity of the solution and η_w the viscosity of water, that factor, with considerable variation, tends to be linear with dose.

Dose adjusted to give equivalent changes. It seemed likely that the best way to obtain a reliable estimate of the relative effect, frozen and unfrozen, was to adjust the dose to produce similar changes in viscosity. This was done approximately for the results in Fig. 3. The relative number of passes was varied from 1/4 (1 pass at a belt speed of $4 \times 2 = 8$ cm/sec) for temperatures above 0°C to 5 (5 passes at a belt speed of 2 cm/sec) for temperatures below 0°C. There was some variation in the changes in
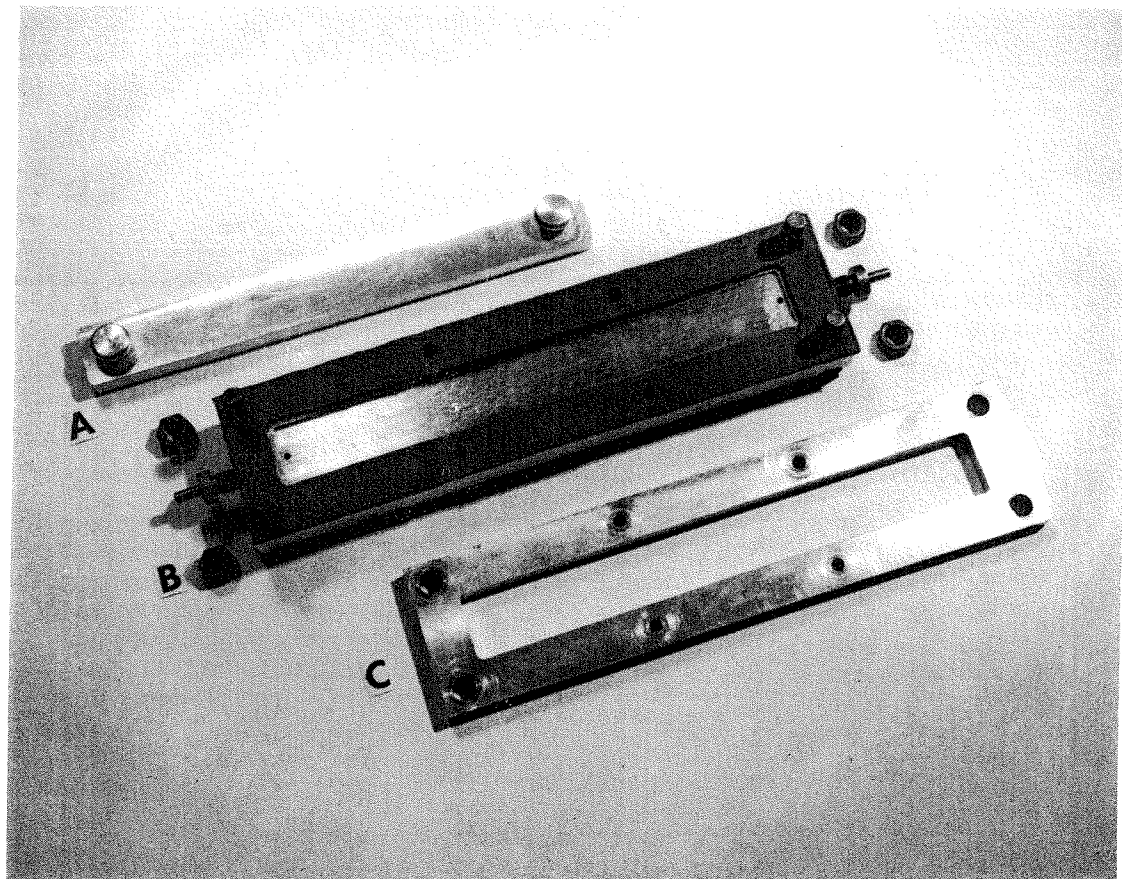
FIG. 1. Irradiation cell. (A) Removable cell cover. (B) Cell body shown with gasket. Aluminum foil that goes between gasket and cell not shown. (C) Cell top section. (A) fits inside (C) and rests on aluminum foil within gasket.
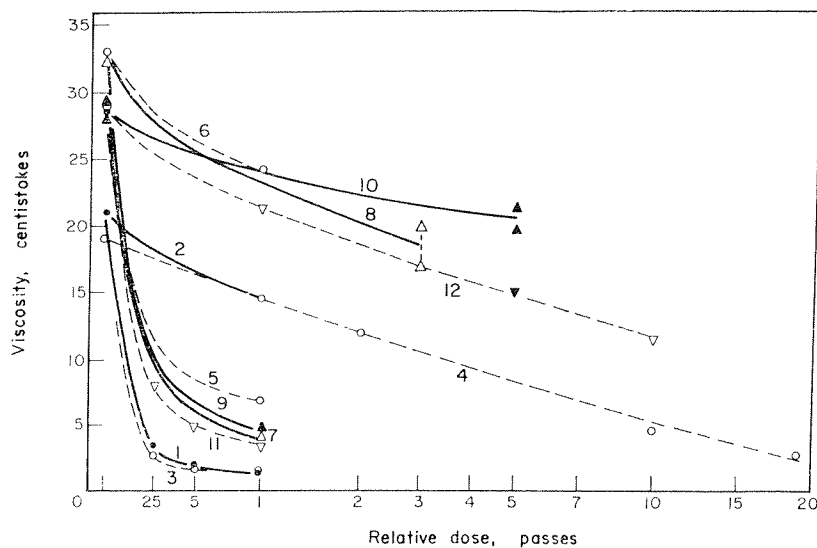
FIG. 2. The change in viscosity of CMC solutions on irradiation at temperatures above and below freezing. Preliminary results 1–4 irradiated at 1% concentration; others at 3% concentration. Odd numbered curves irradiated at room temperature; even numbered curves irradiated frozen. All measured at 1% concentration, at 20°C.
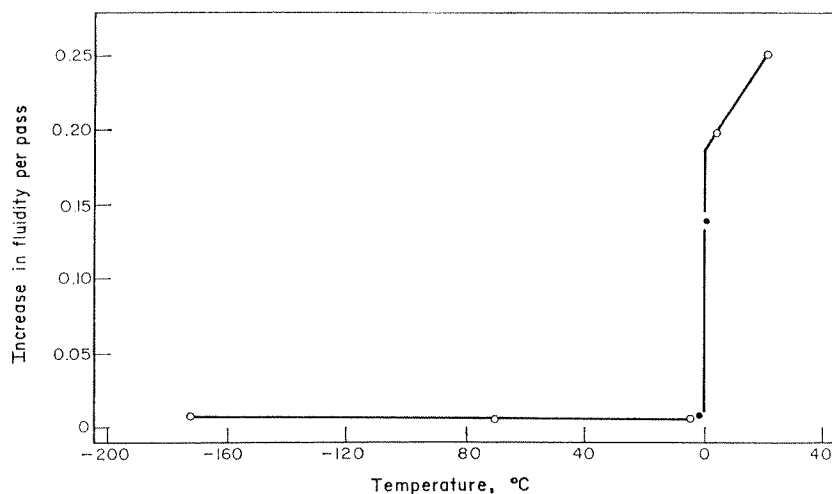

FIG. 3. The increase in fluidity of CMC solutions per pass as a function of temperature. Filled circles represent preliminary results.

viscosity. For the control samples the viscosity was 31.6 centistokes; for the irradiated samples it varied from 10·1 to 8.3 centistokes. The change varied from 21.5 to 13.3.

The ordinate in Fig. 3 is the increase in specific fluidity per pass, i.e. $\Delta[1/(\eta/\eta_w - 1)]/N$ where η is the viscosity of the solution and η_w is the viscosity of water and N is the relative dose

in passes under the beam at a belt speed of 2 cm/sec. The curve was drawn with a sharp break at 0°C but the data are not adequate to insure that the break is that sharp or that it occurs exactly at 0°C. There is apparently a definite increase with temperature above 0°C. The striking effect, though, is the break near 0°C. The rate of producing change in the polymer

TABLE 1. Effect of oxygen on CMC

Irradiation temperature	Concentration during irradiation (%)	Relative dose	Viscosity, Argon	centistokes/sec Oxygen
Room	1	0	21	19
		$\frac{1}{4}$	3.4	2.7
		$\frac{1}{2}$	1.9	1.7
		1	1.4	1.5
	3	0	33.1	
		1	6.8	
	3	0	30.5	
		1	4.0	
	3	0	28.7	
		1	4.4	
	3	0		28.7
		$\sim\frac{1}{4}$		8.0
		$\sim\frac{1}{2}$		5.0
		1		3.5
	3	0		31.6
		$\frac{1}{4}$		13.9
Frozen	1	0	21.0	19.0
		1	20.4	14.5
		2	11.9	
		10		4.6
		20		2.8
	3	0	33.1	
		1	24.2	
	3	0	30.5	
		3	18.9	
	3	0	28.7	
		5	20.5	
	3	0		28.7
		1		21.2
		5		15.1
		10		11.5
	3	0		31.6
		5		17.2

is about 37 times as great in the liquid as in the frozen material. A similar plot of the change in viscosity per pass shows a corresponding change of $\sim 24/1$; possibly the two values would be somewhat closer if the dose had been adjusted more carefully.

Effect of oxygen. A fairly large effect of oxygen was expected but since the first measurements showed a relatively small effect, the extent has not been accurately determined. The results, all under somewhat similar conditions except the conditioning in argon or oxygen, are summarized in Table 1. The reduction in viscosity is probably somewhat greater in oxygen than in argon for room temperature irradiation; possibly it is also for frozen samples.

Nature of the changes in CMC. The effect of radiation on CMC seems to be solely chain

scission. On centrifuging, the samples showed no gel fraction, before or after irradiation.

Gelatin

Preliminary results. One of the early tests on gelatin gave the results in Table 2. Again there was a very great difference between the effects at room temperature and when frozen. The effect is very non-linear with dose and it is difficult to estimate the magnitude of the difference from these results.

TABLE 2. Preliminary experiments on irradiation of gelatin concentration of initial solution $\sim 5\%$

| Relative | Gel fraction | |
No. of passes	Room temperature	Frozen
$\frac{1}{4}$	0.012	
$\frac{1}{2}$	0.20	0.004
1	0.62	0.032
2		0.36

Attempts to adjust dose to give equivalent changes. The solid curve in Fig. 4 shows the amount of gel produced per pass at a belt speed of 2 cm/sec. The attempt to adjust the dose to produce the same amount of gel was not very effective. Below 0°C, only at −20°C did the amount of

gel approach the amount produced above 0°C. Because of this small amount of gel it is difficult to compare the effects above and below 0°C quantitatively. CHARLESBY[11] showed by theory and experiment, that $s + \sqrt{s}$ where s is the sol fraction, is linear or nearly so with the reciprocal of the dose. For the present results this seems to be the case only for small s, i.e. for fairly large doses, and this method of plotting does not seem to be very useful. However, below 0°C, all the points in Fig. 4 are too low relatively, much so for all except those at −20°C and the following procedure was followed in an attempt to overcome this error.

For the results in Table 2 and some of those in Fig. 4, the gel fraction, g, increases as a fairly high power of the dose; with considerable fluctuation, it seems that $g \alpha N^{5/2}$. For all the samples above 0°C, the average value of g is ~ 0.7. Assuming the 5/2 power, the extrapolated value of N to make $g = 0.7$ was calculated from the measured value of N at the lower values of g. The value of g/N was calculated by dividing 0.7 by the extrapolated value of N and those values are shown without the individual points by the broken line in Fig. 4. With this correction, from 0°C to −70°C, the
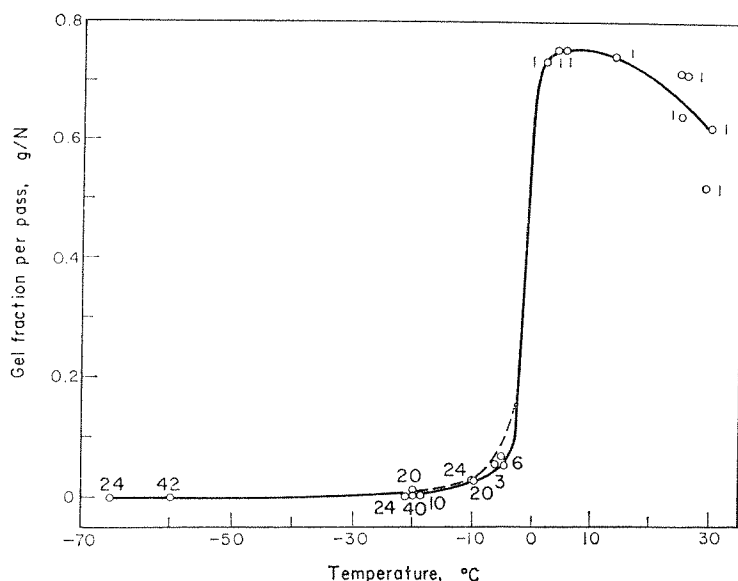

FIG. 4. The gel fraction of gelatin per pass as a function of temperature. Solid curve as measured. Dashed curve, corrections made to take account of the small amount of gel produced at low temperature. Numbers beside points indicate number of passes.

absolute extrapolated values are higher but on the scale of Fig. 4, this is evident only at −5 and −20°C. Even with the uncertainties in the extrapolations, the broken curve is no doubt a better representation of the effect of temperature. Although the change on freezing is great, the break near 0°C is not as sharp as for CMC. The rate at +5°C is ∼ 7.5 times as great as at −5°C. Between −5 and +5°C, the rate changes rapidly but smoothly. Below −5°C the rate tends to decrease considerably. On the 5/2 power assumption, it appears that 200 or more passes would be needed to make $g = 0.7$ at −60 to 70°C.

The production of active centers is probably mainly or wholly by direct target hits over the whole range of temperatures below 0°C but the cross linking involves the further action of motion of two active centers to effect combination. The latter process depends on the mobility of the polymer chains and this likely decreases as the temperature decreases.

The curve as drawn above 0°C is also complicated. It may be that all the points show the same gel fraction within experimental error but the maximum could very well be a real effect. In this temperature range the mobility of the polymer chains is involved. In this case, however, the major effect is indirect, from active particles produced by reaction with the water and the polymer chains are in competition with more mobile particles which do not enter into cross linking. The extent of cross linking could very well decrease with increase in temperature.

Nature of change in gelatin. An attempt was made to learn more about the process in gelatin by measuring the viscosity of the fraction not gelled. The results are fragmentary but perhaps significant. For frozen samples, the viscosity of the supernatant liquid was slightly less than that of the control, whether the amount of gel was slight or as much as 0.25. For room temperature samples the results were more complicated. For a very small amount of gel the viscosity of the supernatant decreased slightly. For a little more gel the viscosity increased slightly. There was some cross linking rather early, not enough for significant gelling, but enough to increase the viscosity. Apparently along with the production of active centers or possibly closely connected with that process, there was some chain scission. At low temperature even with some cross linking, some short chains remain; at room temperature apparently they disappear fairly rapidly. In the final result, with significant amounts of cross linking not much evidence of chain scission remains.

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